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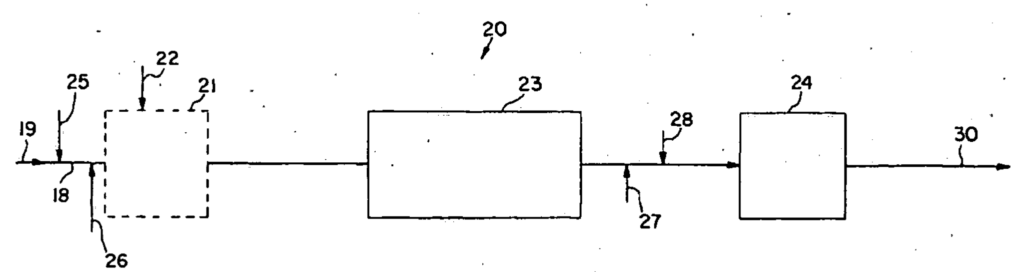

(57) Abstract: Raw water is treated with chlorine, chlorine dioxide and ammonia in various stages as it proceeds from raw water acquisition through clarification (coagulation, flocculation, sedimentation, and filtration) to storage of finished water from which the treated water can be introduced into a distribution system. Chlorine dioxide can be used as a pre-oxidant or disinfectant. Chlorine can be used as a disinfectant or to react with ammonia to product monochloramine.

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METHODS OF TREATING WATER USING COMBINATIONS OF CHLORINE DIOXIDE, CHLORINE AND AMMONIA

BACKGROUND OF THE INVENTION

The present invention pertains to treatment of drinking water and in particular the use of chlorine dioxide, chlorine, ammonia and mixtures thereof in various stages of currently used drinking water treatment processes.

Chlorine, chlorine dioxide, ozone and monochloramine are the chemical disinfectants most commonly used in treating drinking water. Sodium hypochlorite is sometimes used in place of chlorine gas to produce essentially the same chemical effects in the drinking water as chlorine. Monochloramine (NH_2Cl) is created mixing chlorine and ammonia, typically by injection of chlorine into water containing an excess amount of ammonia (i.e. more than two moles of ammonia per mole of chlorine injected).

In addition to the foregoing, other chemicals such as potassium permanganate also serve as oxidants in drinking water. Oxidants can aid in removal of dissolved metals, and destruction of some problem organic compounds.

In a typical drinking water plant, raw water is drawn from a lake, reservoir, river, stream, underground aquifer, or other body of water. Various chemicals are added to the raw water to oxidize contaminants, achieve disinfection, and/or enhance removal of solids during subsequent process steps. The water is then subjected to various solids-removal steps which typically include coagulation, sedimentation and filtration. Solids removal may alternatively be achieved through other processes such as dissolved air flotation, membrane separation, or others. Following solids removal, the water typically flows to a finished water storage facility and then to a distribution system.

The effectiveness of disinfection in drinking water is a function of the concentration of the disinfectant multiplied by the time the disinfectant is in contact with the pathogens. A common measure of the level of disinfectant is the phrase CxT (concentration multiplied by contact time). Since the concentration of a disinfectant declines as it reacts with contaminants in the water and the degree of disinfection at a given relationship of contact time multiplied by concentration (CxT) is a function of many variables such as temperature and pH, there are complex rules for calculating CxT. There are guidelines and

regulations governing what levels of CxT are required for safe drinking water. Each disinfectant has different guidelines for the CxT required to achieve certain levels of disinfection for each type of pathogen, (e.g. virus, bacteria, encysted parasites).

Historically, drinking water treatment plants have used chlorine as an oxidant and disinfectant. Chlorine, however reacts with organic compounds in the water to produce halogenated by-products, such as, trihalomethanes (THM's) and haloacetic acids (HAA's). There is increasing evidence to show that these compounds are carcinogenic. There is also increasing evidence to show that these compounds cause a number of other health problems such as an increase in the rate of miscarriages among pregnant women. Government regulations continue to lower the maximum allowable levels of these compounds in drinking water.

Chlorine dioxide does not produce THM's or HAA's when used in the treatment of drinking water. Since chlorine dioxide does not chlorinate, rather it oxidizes material through an electron transfer mechanism, when added to natural water for the purposes of oxidation and/or disinfection, it does not produce regulated halogenated by-products. Compared to free chlorine, chloramines have less oxidation potential. Because chloraimes do not react as quickly with organic material as free chlorine, the amount of halogenated by-products produced are significantly lower. Ozone does not produce THM's or HAA's but it can produce problem by-products such as bromate, depending upon the composition of the water and ozone is often more expensive to use than other oxidants.

SUMMARY OF THE INVENTION

Chlorine, chlorine dioxide and ammonia, as gases or aqueous solutions, can be used in various combinations in the process of treating drinking water. Chlorine dioxide can be used as an oxidant and as a disinfectant. For either purpose it can be introduced into early or later stages of the water treatment process.

Chlorine dioxide for treatment of drinking water is typically produced by reacting chlorine and sodium chlorite, as taught in U.S Patent 5,110,580. Chlorine dioxide can be produced at lower cost through other processes such as acidification of sodium chlorate ($NaClO_3$). However, this lower-cost chlorine dioxide is produced as a mixture with chlorine. In the prior art, it was necessary to separate the chlorine from the chlorine dioxide

and recycle the chlorine using complex and expensive process steps i.e. by the Day-Kesting Process described in Ullman's Encyclopedia of Industrial Chemistry 5th ed. 1986, Wersheim, New York, N.Y. Chlorine, chlorine dioxide, and monochloramine are used in various ways to oxidize contaminants and to disinfect drinking water. Chlorine dioxide and chloramine are used individually in drinking water, but not injected together. Typically chlorine dioxide is injected early in the treatment process while chloramine is formed near the end of the treatment process.

The present invention has at the core using a mixed stream of chlorine and chlorine dioxide, sometimes with ammonia, to disinfect and pre-oxidize drinking water while minimizing production of THM's and HAA's.

All three components can be introduced together into the raw water. The chlorine dioxide provides rapid disinfection and, in the typical application, is rapidly consumed. The chlorine and ammonia combine to form monochloramine which provides slower but long-lasting disinfection and will persist in the water throughout the process into the storage and distribution of the clean or potable water.

Thus in its broadest aspect the present invention is a method of treating water to produce residual monochloramine and ClO_2 in said water comprising the steps of; injecting a mixture of chlorine and chlorine dioxide into the water together with ammonia said ammonia being present in an amount to produce residual monochloramine with substantially no chlorine in the water.

In another aspect the present invention is a method for treating water as it proceeds from a source to a storage or distribution facility comprising the steps of; injecting a mixture of chlorine and chlorine dioxide into the water at a location between the source and the storage or distribution facility; and injecting ammonia into the water, at one of, upstream or downstream of the location where the chlorine and chlorine dioxide are injected into the water, the ammonia being injected in an amount to substantially react with the chlorine, whereby the water in the storage or distribution facility contains chlorine dioxide, monochloramine and a negligible amount of chlorine.

Therefore, in yet another aspect the present invention is a method for treating water using a stream containing chlorine and chlorine dioxide comprising the steps of

separating the chlorine from the chlorine dioxide to yield a stream of chlorine and a stream of chlorine dioxide; using the chlorine dioxide to pre-oxidize a stream of raw water prior to subsequent steps for removal of solids; and using the chlorine to disinfect the water after some solids have been removed from the water but prior to storage for distribution.

Since chlorine dioxide decomposes in sunlight, application of the chlorine dioxide at the entrance to the raw water main can sometimes provide a long, well-mixed, dark vessel (the raw water main) where the chlorine dioxide can effectively react with contaminants.

In a further aspect the present invention is a method for treating and disinfecting raw water comprising the steps of introducing a mixture of chlorine, chlorine dioxide and excess ammonia into the raw water to provide disinfection of the water by chlorine dioxide and creation of monochloramine by reaction of chlorine and ammonia, passing the raw water through further treatment steps wherein solids are removed whereby residual chlorine dioxide is consumed prior to filtration; and collecting a potable finished water containing residual monochloramine to provide residual disinfection of the finished water.

In some situations, it is not economical to disinfect raw water using chlorine dioxide because high levels of contaminants in the raw water consume too much chlorine dioxide before adequate CxT credit is achieved. Some disinfection is needed throughout the plant to suppress biological growth in basins filters. In these cases chlorine and ammonia may be fed into the raw water. The resulting chloramine persists through the entire plant process and serves to suppress biological growth, without producing THM's and HAA's. Substantial amounts of the contaminants are removed during the solid removal steps, after which a relatively smaller dose of chlorine dioxide may be applied to the filtered water to achieve disinfection. This may or may not be done in conjunction with feeding a relatively small dose of chlorine dioxide into the raw water to remove metals, and aid in coagulation/sedimentation.

In yet, a further aspect the present invention is a method of treating contaminated raw water comprising the steps of a) introducing chlorine and ammonia into the raw water to produce residual monochloramine which suppresses biological growth in

the water as it proceeds through subsequent processing steps; b) passing the water from step a) through solids removal processes; and c) treating the water after solids removal and prior to storage with one of chlorine dioxide, a mixture of chlorine dioxide and chlorine, or a mixture of chlorine dioxide, chlorine and ammonia for disinfection.

In still another aspect of the present invention is a method of treating raw water using streams of chlorine dioxide, chlorine and ammonia comprising the steps of a) introducing chlorine dioxide into raw water in a raw water main; b) subjecting the raw water containing chlorine dioxide to solids removal processes; c) introducing additional chlorine dioxide into the water as it is withdrawn from the solids removal process and conducted to finished water storage; and d) introducing chlorine and ammonia into water withdrawn from storage for distribution to users to provide monochloramine in the water by reaction of chlorine and ammonia.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic representation of a typical drinking water purification process.

Figure 2 is a schematic drawing of a typical water purification plan using a total chlorination scheme.

Figure 3 is a schematic representation of a basic process according to the present invention.

Figure 4 is a schematic representation of application of the processes of the present invention in a water treatment process.

Figure 5 is a schematic representation of a process according to the present invention using chlorine dioxide pre-oxidation and chlorine disinfection.

Figure 5a is a schematic representation of an alternate method of using a mixed chlorine/chlorine dioxide stream in the process of Figure 5.

Figure 5b is a schematic representation of an alternate method of further treating the dilute mixed stream of chlorine dioxide and chlorine in the process of Figure 5.

Figure 6 is a schematic representation of a process according to the present invention using a combination of chlorine dioxide and monochloramine for total disinfection and oxidation.

Figure 7 is a schematic representation of a process according to the present invention using combined chlorine dioxide/monochloramine disinfection with oxidation and disinfection boost in finished water storage.

Figure 8 is a schematic representation of a process according to the present invention using chlorine dioxide pre-oxidation and disinfection with monochloramine as a residual disinfectant.

DETAILED DESCRIPTION OF THE INVENTION

A conventional drinking water purification process shown as 100 in Figure 1 involves a source of water 112 which can be a lake, river, reservoir, aquifer or other body of water. Water from the source 112 enters an intake structure 114. Depending upon the relative elevation of the water source 112 and the treatment facility the water then flows by gravity or is pumped through a raw water main 116 to a rapid mix tank 118 where chemicals such as pH adjusters, coagulants and disinfectants are added. The water then flow through a suitable conduit 120 into flocculation and sedimentation apparatus 122 where slow mixing causes solids to coagulate and settle to the bottom of the tank where they are removed as shown by arrow 124. In some plants coagulated solids are removed through other processes such as dissolved air flotation. The settled water then flows through a suitable conduit 126 into a filter system 128 where it is passed through beds of sand, crushed anthracite or other granular materials. In some plants filtration is achieved by forcing the water under pressure through membranes. Fine suspended solids are removed by the filter medium. When the filter medium becomes filled with solid particles, it is back washed to remove the solids as shown by arrow 130. The clean water from the filtration step 128 is then moved by suitable conduit 132 into a finished water reservoir or storage facility 134. Water can be withdrawn from the finished water storage 134 and introduced into a distribution piping system which includes a primary main 136 secondary mains 138 and laterals 140 for introduction into individual users homes or businesses.

There are many variations on the basic process used to treat drinking water. In many applications, chlorine and chlorine dioxide interact in synergistic ways to accomplish disinfection of the water. As chlorine dioxide reacts with contaminants, it forms Cl^- and chlorite ions (ClO^-_2). Typically the amount of chlorite ion produced is equal to about 50 to 70% of the weight of the chlorine dioxide. In the presence of chlorine, the chlorite is converted back to chlorine dioxide. Thus chlorine dioxide is regenerated. In the distribution system the regeneration of chlorine dioxide can cause minute quantities of chlorine dioxide to be released into homes when the water is running. This usually is not a problem. However, in the presence of new carpet, new paint or other sources of volatile organic compounds (VOC's), the interaction of chlorine dioxide and VOC's produces a very strong and objectionable odor. This odor-causing reaction is well documented but not well understood.

Therefore, the level of chlorite entering the distribution system should be maintained below a low level (e.g. 0.2 mg.), if chlorine is used as a residual disinfectant in the distribution system. In such a case the maximum acceptable level of chlorite ion entering the distribution system is a function of many variables such as water chemistry, temperature, and retention time in the distribution system. Since chlorine dioxide reacts very quickly with contaminants in the water, the residual chlorine dioxide in the finished water leaving the water treatment plant is usually far below the problem level. However, if chlorine is used for residual disinfection, the chlorine may react with chlorite ions to regenerate chlorine dioxide in the finished water long after the water leaves the plant. There are two solutions to this problem. These are:

1. Remove the chlorite ion after the chlorine dioxide has accomplished its function. This is established technology, and may be necessary if high doses of chlorine dioxide are required, which produce chlorite levels above the regulated limit of 1ppm.

2. Use monochloramine for residual disinfection. Monochloramine does not react with chlorite ion to regenerate chlorine dioxide in the distribution system.

Although monochloramine is a weaker disinfectant than chlorine, monochlorine is sometimes preferred over chlorine for residual disinfection in the distribution system. This is especially true in areas of the country where there are very long distribution pipes. Monochloramine dissipates much more slowly than chlorine and maintains a more reliable residual disinfection in distribution systems with long retention times. In some water, chlorine reacts with compounds such as phenols to produce noxious, bad smelling compounds. Monochloramine and chlorine dioxide do not produce these odors. Also, monochloramine reacts much slower with organic material than does chlorine, thereby reducing the production of THM's and HAA.

Figure 2 is a schematic representation of a typical approach to oxidation and disinfection in a typical drinking water plant. If the incoming water contains certain kinds of contaminants, pre-oxidation may be required in order to achieve this. Chlorine as shown by arrow 150 may be introduced into the raw water main or as shown by arrow 152 into the rapid mixed tank 118 chlorine may also be injected into the settled water before the filters as shown by arrow 154 to prevent biological growth in the filters. Any combination of these injection points is possible. Chlorine as shown by arrow 156 may be injected as the water flows into the finished water storage facility 134. The chlorine introduced into the finished water provides added disinfection and boosts the residual chlorine that is carried into the distribution system 136, 138, 140. If desired, ammonia may be added prior to the distribution in the main 136 if monochloramine is desired in the water to be delivered to the users.

The amount of THM's and HAA's formed during chlorination is a function of the type and concentration of organic precursors in the treated water as well as the concentration of chlorine and the reaction time available. Because of concerns about THM's and HAA's, many plants will not be able to use chlorine in the raw water in the future and many will not be able to use it in the later stages of treatment. Therefore, in most plants new treatment approach must be devised.

In its broadest aspect the present invention is a process for treating raw water as shown schematically in Figure 1. In Figure 1 box 10 represents a quantity of raw water. The raw water is treated by introducing chlorine 12 and chlorine dioxide 14 into the water

10 along with a quantity of ammonia to react with the chlorine to produce residual monochloramine without leaving more than a trace quantity of chlorine in the water. The chlorine dioxide removes contaminants and disinfects the water while the monochloramine persists for long term disinfection of the water 10.

Figure 4 schematically illustrates treating water in a continuous process 20 according to the present invention. The process 20 takes raw water represented by arrow 19 through an intake or main 18 where a mixture of chlorine and chlorine dioxide represented by arrow 26 and ammonia represented by arrow 25 are added. Depending upon the contaminants in the water, the water containing oxidants can be passed through an optional step 21 where other chemicals, such as coagulants, pH adjusters etc., represented by arrow 22 are introduced into step 21. Thereafter the partially treated raw water is subjected to solids removal represented by box 23, which may include, e.g. sedimentation, filtration, dissolved air flotation membrane separation, etc. Water exiting the solids removal step 23 is conducted directly to a distribution system or storage represented by box 24. According to the present invention ammonia represented by arrow 25 and chlorine and chlorine dioxide represented by arrow 26 may be introduced into the water prior to entering the solids removal step 23. In many cases, treatment of raw water will involve using a pre-oxidant step prior to the solids removal step. In these cases the ammonia 25 and chlorine and chlorine dioxide 26 are introduced during this step. At this stage the chlorine reacts with the ammonia to produce monochloramine that will persist in the water through solids removal, storage, and/or distribution and chlorine dioxide provides immediate disinfectant to the water as would available chlorine. Monochloramine provides some level of disinfection throughout the overall process and would help to prevent algae grow in the solids removal equipment.

Alternatively ammonia represented by arrow 27 and chlorine and chlorine dioxide represented by arrow 28 can be introduced after the solids removal step to provide the same effects as discussed above. In certain cases the process can include introducing ammonia and chlorine and chlorine dioxide both before and after the solids removal step.

Figure 5 is a schematic representation of another variation of such a new water treatment process according to the present invention used with conventional drinking water treating equipment.

In the process of Figure 5 a mixture of chlorine and chlorine dioxide represented by arrow 160 is sent to a separation facility 162 which yields a first stream of chlorine dioxide with negligible amounts of chlorine represented by arrow 164 and a second stream of chlorine represented by line 166. There are known process for separating chlorine from chlorine dioxide any of which can be used effectively with the present invention. As shown in Figure 5 the chlorine 166 and chlorine dioxide 164 are two disinfectants used at different points in the water treatment process. In some processes (plants), (depending upon the water chemistry) chlorine can be used without creating THM's or HAA's above acceptable limits if the chlorine is applied after the water has been partially or wholly treated. This is because some of the precursors for THM/HAA formation are removed or oxidized in the treatment process. Therefore, according to the present invention the chlorine dioxide is introduced early in the process and preferably into the raw water main 116 and the chlorine is introduced into the filtered water in conduit 132 or the settled water in conduit 126. In the process of Figure 5 chlorine dioxide applied to the raw water achieves oxidation and some disinfection. Chlorine applied to the water after filtration achieves additional disinfection. Since THM and HAA formation is a function of time, sometimes chlorine can be applied before the filters where it also suppresses biological growth in the filters. Retention time in filters is typically very short, whereas retention time in flocculation and sedimentation is inherently long. The chlorine uses the contact time with the finished water storage to achieve additional CxT credit and to accomplish residual disinfection. Ammonia can be introduced as shown by arrow 90 into the finished water in conduit 136 prior to being distributed to produce monochloramine in the distribution system in order to provide long term disinfection.

In another aspect of the invention, some or all of the mixed chlorine/chlorine dioxide stream may be converted to chlorine dioxide by passing mixed stream through a porous bed of solid sodium chlorite according to the process disclosed and claimed in U.S. Patent 5,110,580 the specification of which is incorporated herein by reference. The chlorine will be converted to chlorine dioxide and the chlorine dioxide will pass through the process unchanged.

As shown in Figure 5a the entire mixed chlorine/chlorine dioxide stream 160 can be sent to a unit 163 containing a porous bed of solid sodium chlorite wherein the

chlorine is converted to chlorine dioxide as taught in the '580 patent and the chlorine dioxide passes through the bed unchanged into the product stream 165. The product stream 165 from reactor 163 will be substantially pure chlorine dioxide for injection into the raw water as shown in Figure 5. This alternative process lends itself to those applications where there is a separate supply of chlorine available for use in treating the water after oxidation and partial disinfection using chlorine dioxide.

In Figure 6b the gas separation facility 162 produces a stream 164 of chlorine dioxide containing negligible amounts of chlorine and a stream 166 containing chlorine. A portion of the inlet stream 160 of chlorine and chlorine dioxide can be sent to unit 163 containing sodium chlorite wherein the chlorine is converted to chlorine dioxide yielding a chlorine dioxide stream 165 which can be mixed with stream 164 and used in accord with the process of Figure 5.

The chlorine dioxide can be used as a pre-oxidant to partially destroy or reduce THM/HAA precursors. If enough of the precursors are destroyed, chlorine may then be applied without creating unacceptable levels of THM's or HAA's.

According to the present invention, another aspect is to produce a water stream containing a mixture of dissolved chlorine dioxide and monochloramine. The resulting chlorine dioxide/monochloramine stream is ideal for disinfection in many water treatment plants. Chlorine dioxide is a very rapid disinfectant, but is not accepted in some countries as a residual disinfectant in the water distribution system. Monochloramine is a very slow disinfectant, but provides a long-lasting residual. In some drinking water plants with long retention time, monochloramine can be used as a primary disinfectant. In most cases however, there is not enough retention time for monochloramine to provide primary disinfection. A major drawback to the use of monochloramine as a residual disinfectant is that the excess ammonia sometimes promotes growth of nitrifying organisms in distribution systems. Recent research shows that the chlorite ion, a by-product of chlorine dioxide disinfection, inhibits growth of the nitrifying organisms. Therefore, use of chlorine dioxide in conjunction with monochloramine mitigates the nitrification problem associated with monochloramine residual while use of monochloramine residual solves the problem of odors in homes with new carpets that may occur when chlorine dioxide is used in conjunction with chlorine residual in the water.

Use of chlorine, even in the later stages of the purification process, may be even more limited in the future as limits of THM and HAA are lowered.

Referring to Figure 6 there is shown a process for using chlorine dioxide in conjunction with chloramine in the water treatment scheme. A mixture of chlorine dioxide and chlorine shown by arrow 192 is injected into the raw water in the main 116 with an excess of ammonia represented by arrow 194. The chlorine to ammonia ratio should be at or below 5:1 by weight depending upon the pH of the water. For example in a high pH environment the following reaction takes place: $NH_3 + Cl_2 \rightarrow NH_2Cl + HCl$ and in a lower pH environment the reaction proceeds according to the following equation: $2NH_3 + Cl_2 + 2OH \rightarrow 2NH_2Cl + 2H_2O$. Ideally, the chlorine dioxide/monochloramine is injected as near to the raw water intake as possible so that the volume of the raw water main provides retention time for raw water with the oxidants and disinfectants.

In relatively clean raw water with a very long raw water main, the chlorine dioxide may provide adequate disinfection during the time it travels through the raw water main. If there is a residual of chlorine dioxide at the rapid mix tank 118 much of the residual chlorine dioxide may be lost either through degassing from the rapid mixing, or through photolysis and reaction in the subsequent flocculation and sedimentation step 122. This is because many of the flocculation/sedimentation basins are open to the air. The monochloramine present in the water in the process shown in Figure 6 does not dissipate or experience rapid photo decomposition as does chlorine dioxide. The monochloramine is carried to the rest of the process and into the distribution system 136, 138, 140 where it provides residual disinfection.

In systems where the raw water is more contaminated, the demand for chlorine dioxide in the raw water may be too high to permit adequate economical disinfection in the raw water main. In these cases, a small dose of chlorine dioxide/monochloramine may be added to the raw water main. The chlorine dioxide is added for pre-oxidation, and is typically completely consumed in the raw water or early in the treatment process. The monochloramine is carried through the plant where it provides some disinfection, controls algae growth in open basins and prevents biological growth in the filters.

In this case, as shown in Figure 7 chlorine dioxide and/or chloramine may be added at the entrance to the finished water storage 34 as shown by arrow 196. Since the finished water typically has low chlorine dioxide demand, and the retention time in the finished water storage 134 is typically long a relatively low dose of chlorine dioxide in the finished water may provide adequate CxT for primary disinfection, if the monochloramine remaining from injection in the raw water is not adequate. Monochloramine injected into the finished water storage will mostly be carried on as a residual in the distribution system.

As shown in Figure 8 separate streams of chlorine dioxide and chlorine can be used in the process. The chlorine dioxide represented by arrow 200 can be introduced into the raw water main 116 while chlorine represented by arrow 202 can be introduced into the water as it enters the finished water storage and 134. In addition, chlorine represented by arrow 204 and ammonia represented by arrow 206 can be introduced into the delivery main 136 for finished water to create monochloramine in the finished water which is being delivered to points of use.

A number of water plants are planning to convert from the use of chlorine as a disinfectant to a combination of chlorine dioxide and monochloramine disinfectant using hauled-in chlorine and chlorine dioxide generators such as the type offered for sale by CDG Technologies Inc. of Bethlehem, Pennsylvania. At one plant that was using chlorination until recently, chlorinated organics (THM's) in the finished water were typically greater than 170 micrograms per liter compared to a regulatory limit of 100 micrograms per liter. This limit will be reduced to 80 micrograms per liter during the year 2001. A chlorine dioxide generator was installed in this plant to oxidize raw water in conjunction with traditional chloramination to achieve disinfection in the finished water. As a result THM's were reduced to below 5 micrograms per liter.

Applicants have shown several new processes for using mixed streams of chlorine, and chlorine dioxide in conjunction with ammonia in the treatment of drinking water that overcome the various problems with prior art processes.

Applicants, can by various process schemes, provide water with residual disinfectant that contains harmful by-products well below regulatory limits, promotes no deleterious or harmful odors and is safe for consumption.

Having thus described our invention, what is desired to be secured by Letters Patent of the United States is set forth in the appended claims, which should be read without limitation.

What is Claimed:

1. A method of treating water to produce residual monochloramine and ClO_2 in said water comprising the steps of:

injecting a mixture of chlorine and chlorine dioxide into said water together with ammonia said ammonia being present in an amount to produce residual monochloramine with substantially no chlorine in said water.

2. A method according to claim 1 including the step of storing a portion of said water containing chlorine dioxide and chloramine for use as a water treatment solution.

3. A method of preparing a water treatment solution for use in treating drinking water comprises the step of:

accumulating a volume of said water to be treated;

injecting a mixture of chlorine and chlorine dioxide into said volume of water together with ammonia, said ammonia being present in an amount to produce residual monochloramine with substantially no chlorine in said water.

4. A method for treating water as it proceeds from a source to a storage or distribution facility comprising the steps of:

injecting a mixture of chlorine and chlorine dioxide into said water at a location between said source and said storage or distribution facility; and

injecting ammonia into said water at, one of, a point upstream or downstream of said location where said chlorine and chlorine dioxide are injected into said water, said ammonia being injected in an amount to substantially react with said chlorine, whereby said water in said storage or distribution facility contains chlorine dioxide, monochloramine and a negligible amount of chlorine.

5. A process according to claim 4 including the step of establishing the chlorine to ammonia ratio at or below 5:1 by weight.

6. A process according to claim 4 including the step of injecting the ammonia downstream of the chlorine/chlorine dioxide injection point, but sufficiently close to the chlorine/chlorine dioxide injection point so that substantially all of the chlorine is above acceptable limits.

7. A process according to claim 4 wherein the water is a contaminated raw water and the treatment process includes the step of applying the ammonia/chlorine/chlorine dioxide stream to the raw water before other treatment steps.

8. A process according to claim 4 including the steps of injecting the chlorine dioxide early enough in the process so that ClO_2 is at an acceptable level for entry into the water distribution system.

9. A process according to claim 4 including the step of creating enough monochloramine to be carried through all treatment steps following its creation to provide all or part of the necessary disinfection in a distribution system.

10. A process according to claim 7 including the step of applying the ammonia/chlorine/chlorine dioxide stream in a raw water main near the intake of the main wherein the chlorine dioxide reacts with contaminants as the raw water flows through the raw water main.

11. A process according to claim 4 including the step of using the ammonia/chlorine/chlorine dioxide stream to one of, oxidize contaminants, or disinfect drinking water with production of chlorinated hydrocarbons kept below acceptable levels.

12. A method for treating water wherein a stream containing chlorine and chlorine dioxide is used to treat drinking water wherein the mixed chlorine and chlorine/chlorine dioxide stream (either as gas or in solution) is injected into the water being treated, and where the point of injection is after THM precursor are removed from the water such that the level of chlorinated organics created is less than the desired limit.

13. A method for treating water comprising the steps of:

a) providing a stream containing gaseous chlorine and chlorine dioxide

b) separating the mixed chlorine/chlorine dioxide stream into two streams, the first of which contains chlorine dioxide that is substantially chlorine-free, and the second stream contains chlorine with a lower level of chlorine dioxide than in the original stream;

c) injecting the stream of chlorine into said water being treated at point in the process after removal of sufficient organic material such that the level of chlorinated organics created is at or below an acceptable level; and

d) using the chlorine dioxide stream to oxidize contaminants and disinfect drinking water at a point in the process before sufficient organics have been removed to allow treatment with a stream containing substantial amounts of chlorine.

14. A process according to claim 13 including the step of injecting ammonia into said water containing chlorine entering a distribution system for treated water to convert said chlorine to monochloramine.

15. A method for treating water using a stream containing chlorine and chlorine dioxide comprising the steps of:

separating the chlorine from the chlorine dioxide to yield a stream of chlorine and a stream of chlorine dioxide;

using said chlorine dioxide to pre-oxidize a stream of raw water prior clarification;

subjecting said water after treatment with chlorine dioxide to clarification by one, a combination of, or all of the steps of coagulation, flocculation and sedimentation, filtration; dissolved air flotation, and membrane filtration; and

using said chlorine to disinfect said water after clarification and prior to storage for distribution.

16. A method according to claim 15 including the step of adding ammonia to said water as it is withdrawn from storage for distribution to create monochloramine in said water for distribution.

17. A method according to claim 16 including the step of establishing the initial chlorine to ammonia ratio at or below 5:1 by weight.

18. A method for treating and disinfecting raw or partially treated water comprising the steps of:

introducing a mixture of chlorine, chlorine dioxide and ammonia into said raw or partially treated water to provide disinfection of the water by chlorine dioxide and creation of monochloramine by reaction of chlorine and ammonia;

passing said raw water through a clarification step being, one of, a combination of, or all of coagulation, flocculation and sedimentation, filtration, dissolved air flotation and membrane filtration whereby residual chlorine dioxide is consumed prior to filtration; and

collecting a potable finished water containing any residual monochloramine to provide residual disinfection of said finished water.

19. A method according to claim 18 including the step of adding ammonia and chlorine to said potable water as it is introduced into a distribution system to create monochloramine in said water.

20. A method according to claim 18 including the step of withdrawing a side stream of raw or partially treated water, introducing ammonia, chlorine and chlorine dioxide into said side stream which is then recycled into a main stream of said water.

21. A method according to claim 19 including the step of establishing the initial chlorine to ammonia ratio at or below 5:1 by weight.

22. A method of treating contaminated raw water comprising the steps of:

a) introducing chlorine dioxide and monochloramine into said raw water to cause pre-oxidation by said chlorine dioxide and introduce monochloramine into said water as it proceeds through subsequent processing steps;

b) passing said water from step a) through clarification being, one, a combination of, or all of the steps of coagulation, flocculation and sedimentation, filtration dissolved air flotation and membrane filtration to effect solids removal; and

c) treating said water after solids removal and prior to storage with one of chlorine dioxide, a mixture of chlorine dioxide and chlorine, or a mixture of chlorine dioxide, chlorine and ammonia for disinfection.

23. A method according to claim 22 including the step of introducing said ammonia at each location at a ratio of chlorine to ammonia of 5 to 1 or less by weight.

24. A method according to claim 22 including the step of introducing ammonia into water as it is withdrawn from storage when said withdraw water contains residual chlorine.

25. A method according to claim 24 including the step of introducing said ammonia at a ratio of chlorine to ammonia of 5 to 1 or less by weight.

26. A method of treating water using streams of chlorine dioxide, chlorine and ammonia comprising the steps of:

a) introducing chlorine dioxide into raw water in a raw water main;

b) subjecting said raw water containing chlorine dioxide to clarification being one, a combination of, or all of the steps of coagulation, flocculation and sedimentation, filtration, dissolved air flotation and membrane filtration;

c) introducing additional chlorine dioxide into said water as it is withdrawn from step b) and conducted to finished water storage; and

d) introducing chlorine and ammonia into water entering finished water storage or as it is withdrawn from storage for distribution to users to provide monochloramine in said water by reaction of chlorine and ammonia.

27. A method according to claim 26 including the step of introducing said ammonia into said water in step d) at a ratio of chlorine to ammonia of 5 to 1 or less by weight.

28. A method for treating water processed in a drinking water treatment plant through various process steps including solids removal by introducing a mixture of chlorine dioxide and chloramine into said water after said solids removal step.

29. A method according to claim 28 including the step of preparing said mixture of chlorine dioxide and chloramine by adding ammonia to a mixture of chlorine and chlorine dioxide at a ratio of chlorine to ammonia of 5:1 or less by weight.

30. A method according to claim 28 including the step of withdrawing a side stream of water after said solids removal step, introducing chlorine dioxide and monochloramine into said side stream and injecting said side stream of water with chlorine dioxide and monochloramine into said water downstream of where said side stream is withdrawn.

31. A method according to claim 27 including the step of withdrawing a side stream of water after said solids removal step, introducing chlorine dioxide, chlorine and ammonia into said side stream said chlorine to ammonia ratio being 5 to 1 or less in said side stream and introducing said side stream into said water downstream of where said side stream is withdrawn.

32. A method for treating water comprising the steps of:

a) providing a stream containing gaseous chlorine and chlorine dioxide

b) passing a portion of the gaseous chlorine and chlorine dioxide stream through a porous bed of sodium chlorite to yield a first stream of chlorine dioxide;

c) separating the remaining portion of the mixed chlorine/chlorine dioxide stream into two streams, the first of which contains chlorine dioxide that is substantially chlorine-free, and the second stream contains chlorine with a lower level of chlorine dioxide than in the original stream;

d) injecting the stream of chlorine into said water being treated at point in the process after removal of sufficient organic material such that the level of chlorinated organics created is at or below an acceptable level; and

e) combining the first stream of chlorine dioxide and the stream of chlorine dioxide substantially free of chlorine into a mixed chlorine dioxide stream and using the mixed chlorine dioxide stream to oxidize contaminants and disinfect the water at a point in the process before sufficient organics have been removed to allow treatment with a stream containing substantial amounts of chlorine.

33. A process according to claim 32 including the step of injecting ammonia into said water containing chlorine entering a distribution for treated water system to convert said chlorine to monochloramine.

34. A method for treating water using a stream containing chlorine and chlorine dioxide comprising the steps of:

passing a portion of the stream containing chlorine and chlorine dioxide through a porous bed of sodium chlorite to yield a stream of chlorine dioxide;

separating the remaining portion of the chlorine from the chlorine dioxide to yield a stream of chlorine and a stream of chlorine dioxide containing negligible amounts of chlorine;

combining said stream of chlorine dioxide and said stream of chlorine dioxide containing negligible amounts of chlorine into a mixed chlorine dioxide stream and using said mixed chlorine dioxide stream to pre-oxidize a stream of raw water prior clarification using, one of, a combination of, or all of the steps of coagulation, flocculation and sedimentation, and filtration; and

using said chlorine to disinfect said water after clarification and prior to storage for distribution.

35. A method according to claim 34 including the step of adding ammonia to said water as it is withdrawn from storage for distribution to create monochloramine in said water for distribution.

36. A method according to claim 35 including the step of establishing the initial chlorine to ammonia ratio at or below 5:1 by weight.

37. A method for treating water comprising the steps of:

a) providing a stream containing gaseous chlorine and chlorine dioxide

b) passing the mixed chlorine/chlorine dioxide stream through a porous bed of sodium chlorite to produce a stream of substantially chlorine dioxide;

c) injecting chlorine into said water being treated at point in the process after removal of sufficient organic material such that the level of chlorinated organics created is at or below an acceptable level; and

d) using the chlorine dioxide stream to oxidize contaminants and disinfect drinking water at a point in the process before sufficient organics have been removed to allow treatment with a stream containing substantial amounts of chlorine.

38. A process according to claim 37 including the step of injecting ammonia into said water containing chlorine entering the distribution system to convert said chlorine to monochloramine.

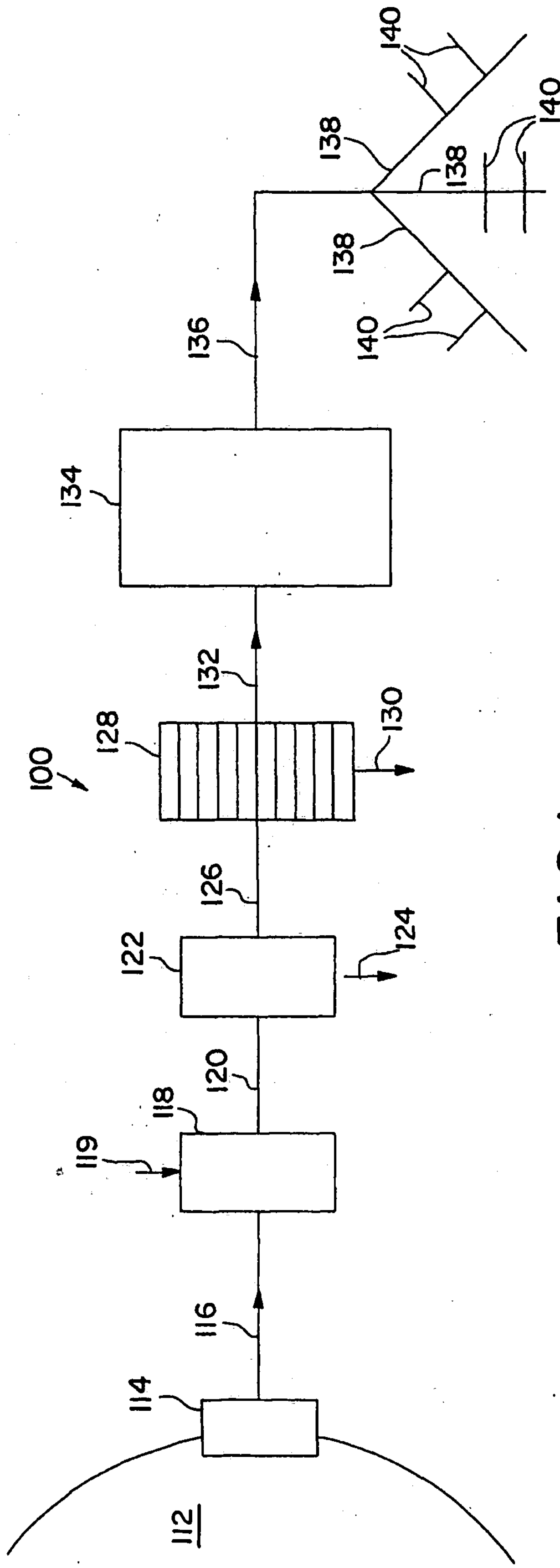

FIG.1
PRIOR ART

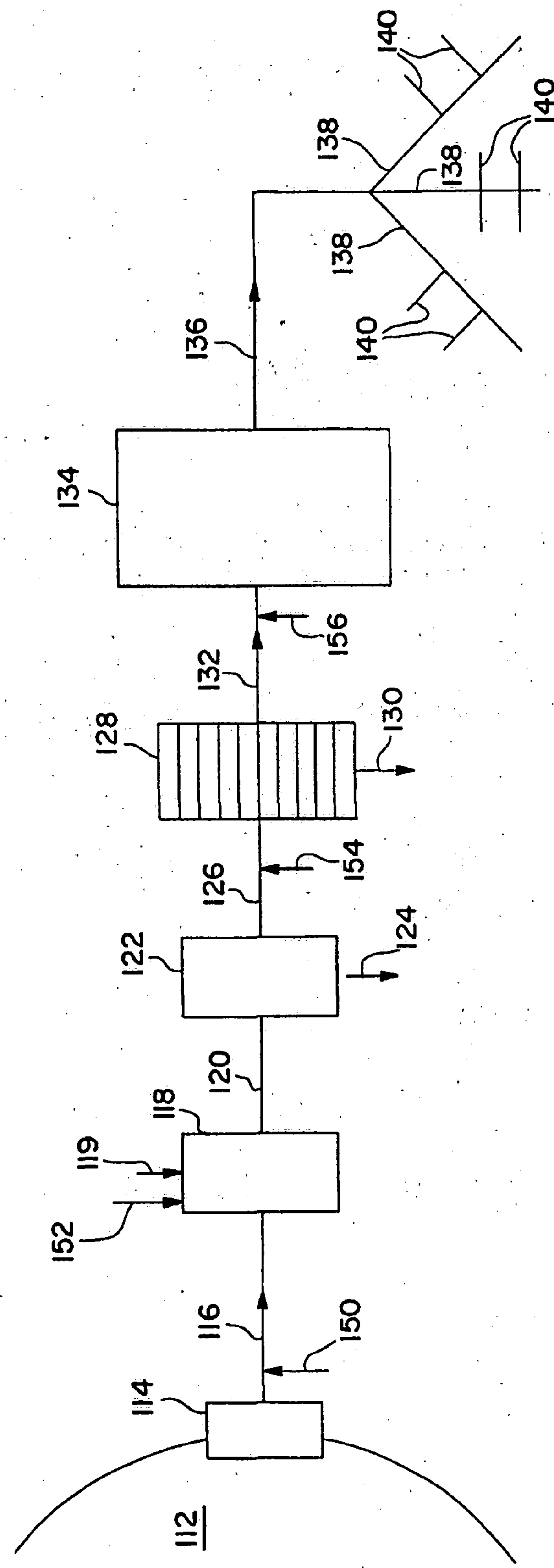

FIG. 2
PRIOR ART

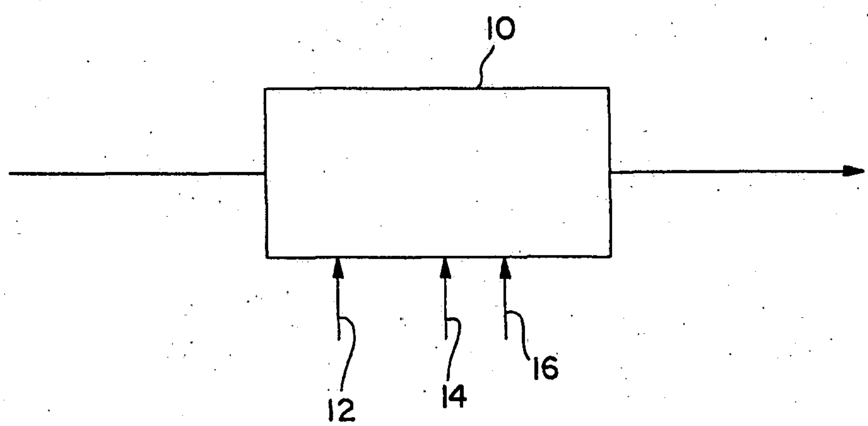

FIG. 3

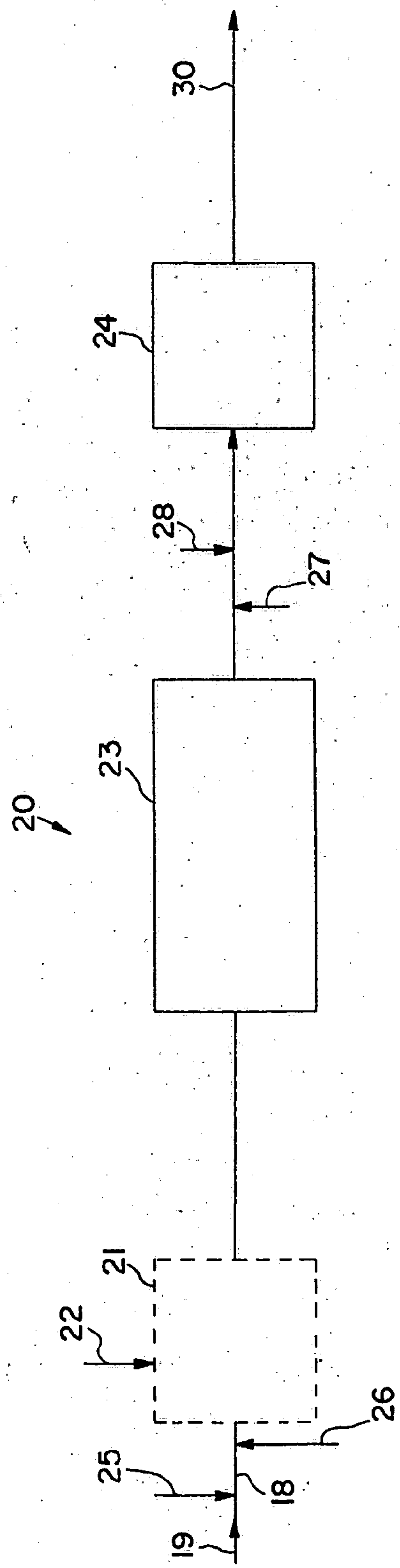

FIG. 4

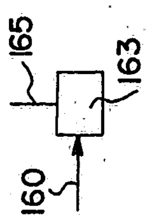

FIG. 5a

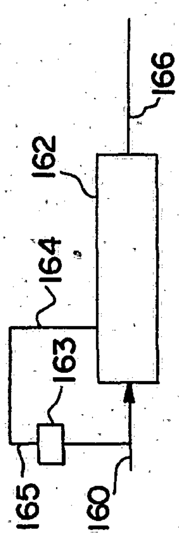

FIG. 5b

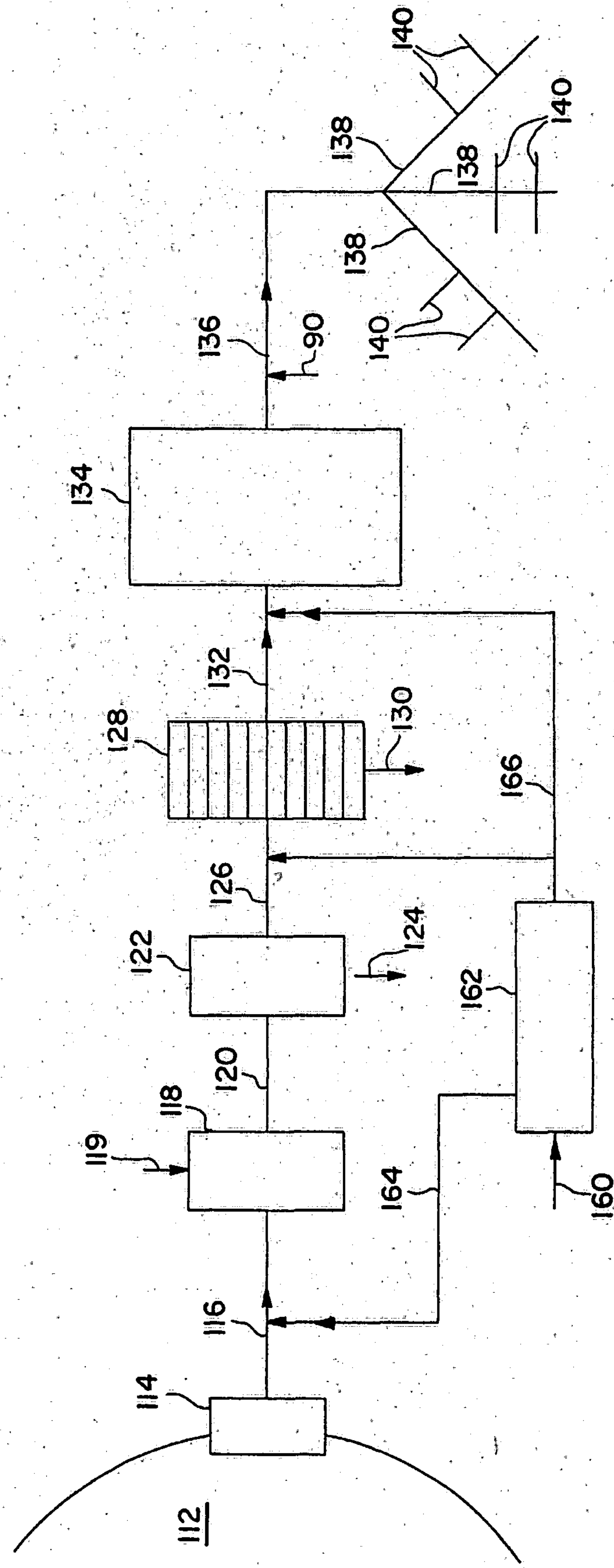

FIG. 5

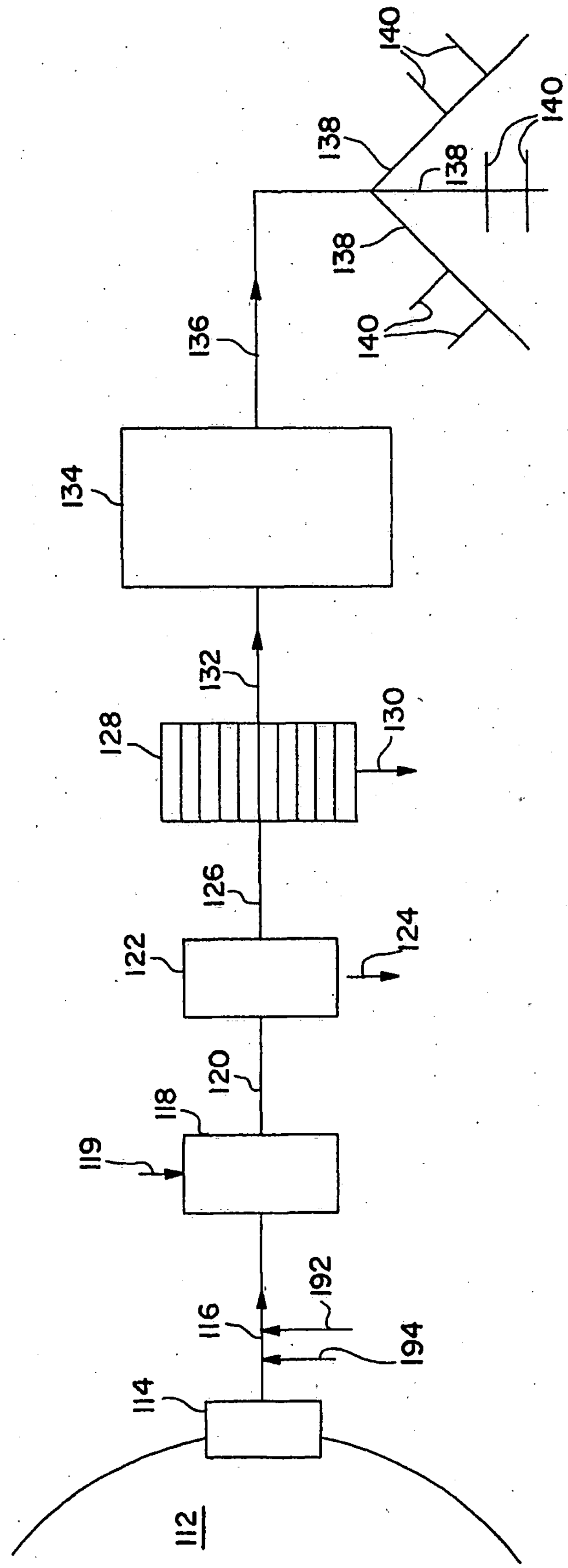
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FIG. 6

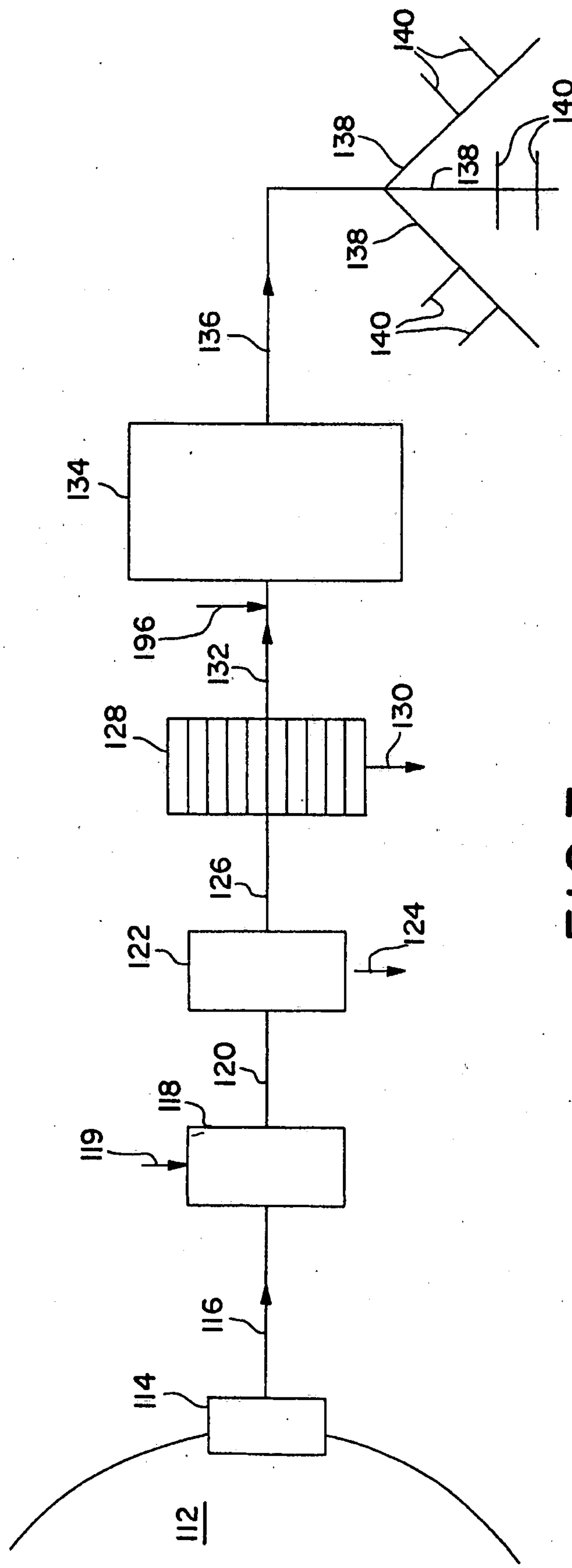
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FIG. 7

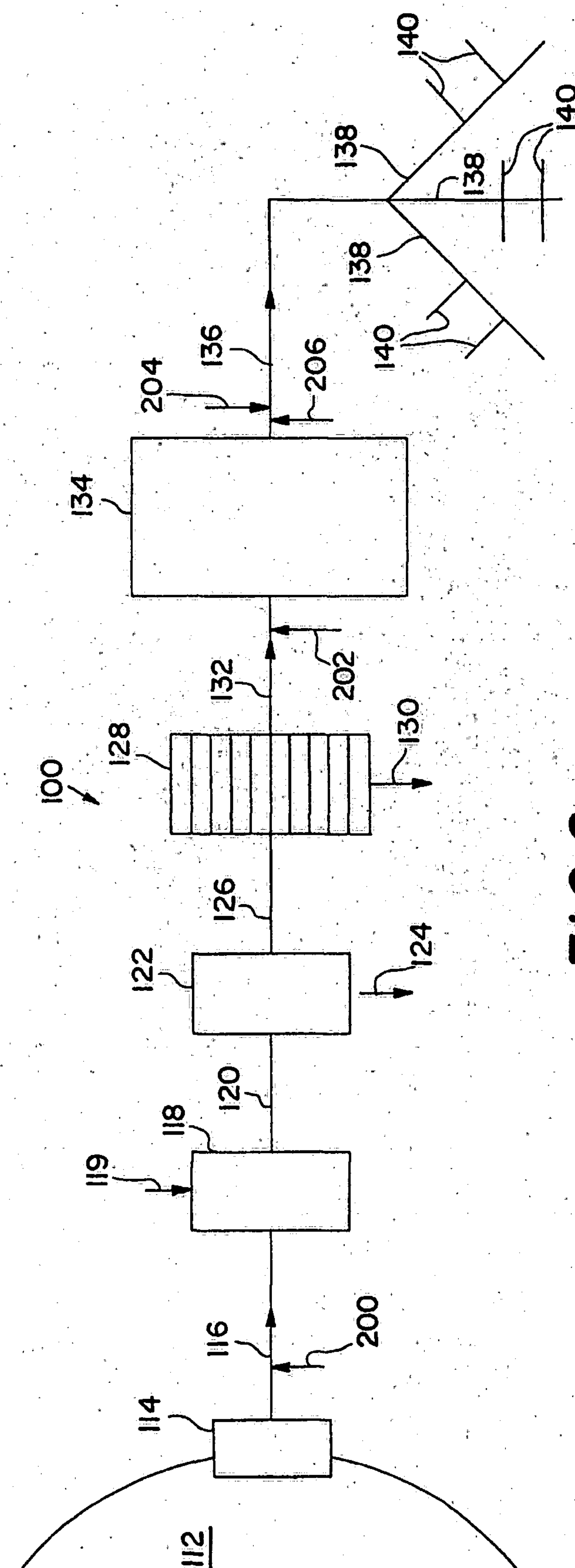
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FIG. 8

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/06061

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C02F1/76

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 975 284 A (LAMBERT MARC) 17 August 1976 (1976-08-17) column 3, line 19-21; claims; figures column 1, line 7-10	1-38

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 July 2002	24/07/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Serra, R

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International application No.
PCT/US 02/06061

INTERNATIONAL SEARCH REPORT

Box I Observati ns where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. [X] Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. [ ] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest.

[ ] No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

In view of the large number and also the wording of the claims presently on file, which render it difficult, if not impossible, to determine the matter for which protection is sought, the present application fails to comply with the clarity and conciseness requirements of Article 6 PCT (see also Rule 6.1(a) PCT) to such an extent that a meaningful search is impossible.

Thirteen independent claims were found in the application, with a set of combinations of features defining water treatment methods wich could comprise one or more of injecting chlorine, injecting chlorine dioxide, injecting ammonia, injecting chloramines and reacting chlorine and ammonia to produce monochloramine in the water to be treated.

the present invention has at the core using a mixed stream of chlorine and chlorine dioxide, sometimes with ammonia, to disinfect and pre-oxidize drinking water while minimizing production of THM's and HAA's.

Consequently, the search has been carried out for those parts of the application which do appear to be clear (and concise), namely the method for treating water comprising the steps of injecting chlorine, chlorine dioxide, and ammonia in order to produce residual monochloramine with substantially no chlorine in water.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 02/06061

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3975284 A	17-08-1976	FR 2140781 A5	19-01-1973